Molecular Electronics

I. Introduction

- The aim of using molecular Nanoelectronics
  - Assembling large number of molecules into Nano-scaled objects to form circuits.
  - Reduce the fabrication costs as well as the energetic costs.
- Problems in molecular Nanoelectronics
  - Control of the molecule-electrode interfaces.
  - Need improvement in reproducibility and reliability.
- Molecules based devices fabricated by a new or already existing function but at simpler process level and lower cost because of their self-organization capabilities.
- In general, molecular electronics is envisioned as a promising candidate for the Nano-electronics of the future.

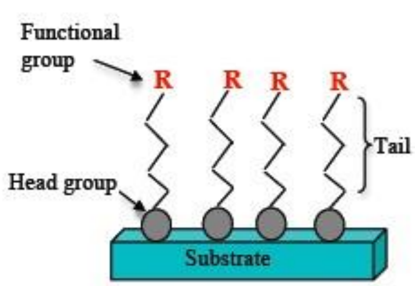
II. Chemistry and Self-Assembly

- Organic monolayers are deposited on the electrodes and solid substrates.

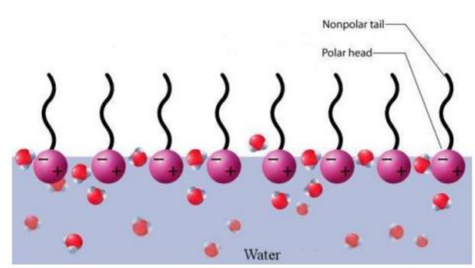
- **Self-assembled monolayers (SAMs)**
  Molecules are formed spontaneously on surfaces by chemisorption
  - Thiol based SAMs on gold
    - Disadvantage: Current level fluctuations
  - SAMs on silicon/silicon dioxide
    - Advantage: More stable bonds

- **Langmuir–Blodgett Monolayers (LB films)**
  - Molecules are formed spontaneously on surfaces by physisorption.

- **SAMs vs. LB films**
  - SAMs are more robust than LB films mechanically and thermally.
  - Chemisorption processes are now more systematically used both for making monolayers and to attach a single molecule between nanoelectrodes.



SAM formation



LB films formation

III. <u>Contacting the molecules</u> "Measuring Conductance"

a. Lab Level

1. STM-BJ (Break Junction)

- Repeatedly forming few thousands of Au-molecule-Au junctions by moving STM Tip.
  - Due to the large number of measurements, this technique provides statistical analysis of the conductance data.
- C-AFM as the upper electrode, the metal-coated tip is gently brought into a mechanical contact with the monolayer surface while an external circuit is used to measure the current–voltage curves.
  - The critical point is the sensitive control of tip load to avoid excessive pressure on the molecules to avoid modifying the molecule conformation and thus its electronic transport properties or even can pierce the monolayer.

2. Mercury Drop

- Organic monolayer electrical properties can be measured by contacting it by mercury drop.

3. Mechanically Breaking Junction (MBJ)

- A small metallic nanowire is fabricated by e-beam lithography on a bendable substrate.
- A drop of solvent with the molecules of interest is placed on the nanowire.
- Nano wire is elongated and broken by bending the substrate forming a nanogap.
- A few molecules can chemically bridge the nanogap and they are electrically measured.

Problems of Lab Level Techniques

- Deposition of metal electrode on the top of an organic monolayer causes
  - Degradation of the monolayer.
  - Metallic shorts.

❖ It is clear that connecting molecules with these laboratory techniques is hard to achieve.

b. Device-Like Level

Problems of metal atoms reactivity with end groups of the molecules

- **Strong Reactivity**
  - Overlayer of metal oxides may perturb the electronic coupling between the metal and the molecule.
- **Weak Reactivity**
  - Metal atoms diffuse through the monolayer to the bottom interface forming an adlayer and metallic shorts.

Techniques developed to solve previous problems

- **Soft metal deposition.**
- **nano-transfer printing (nTP)**
    - Print Nano patterns on solid substrates using soft lithographic technique.
    - Gold electrodes are deposited by evaporation onto an elastic stamp.
    - Gold is transferred by mechanical contact onto a Thiol-functionalized SAM.
    - A thin conducting polymer is introduced as a buffer layer between the organic monolayer and the evaporated metal electrode to avoid formation of metallic filamentary paths.

IV. <u>The molecule/electrode contact challenge</u>

- Electrical conductance of the molecular junction is influenced by
    - Chemical nature of the molecule/electrode contact.
    - Atomic configuration of the molecule/electrode contact.
- Theoretical calculations predicted that “Se” and “Te” are better links than “S” for the electron transport through molecular junctions.
    - “Se”: Selerium, “Te”: Tellurium, “S”: Sulfur.
- The chemical link acts as a tunnel barrier for electron transfer between the electrode and the molecule leading to the following
    - The conductance of a molecular junction is small.
    - Molecular electronics is “high-impedance” electronics.
    - Large power dissipation for a high density of molecular devices in a chip.
- Recently a significant progress was made towards “low impedance” molecular electronics
- Due to relatively large energy offset at the molecule/electrode interface, the conductance is mainly dominated by tunneling.
- Electron transport is limited to few nanometers in these systems.
    - This limitation has been recently overcome by introducing step-by-step, metallic ions.
- Resistance of molecular wire vs. metallic nanowire
    - Molecular wire is in **MΩ** range.
    - Metallic nanowire is in **KΩ** range.
    - Molecular wire high resistance is due to the lack of molecule-contact optimization.

V. Functional molecular devices

1. Charge-Based Memory

- Uses reduction-oxidation (Redox)-active molecules attached on a silicon substrate
- Charging by reduction (gaining electrons).
- Discharging by oxidation (losing electrons).
- Good characteristics:
  - Works at relatively low potentials (below ~1.6 V).
  - Can undergo trillions of write/read/erase cycles.
  - Retain charge for long enough (minutes) compared with semiconductor DRAM (tens of ms).
  - Extremely stable under harsh conditions (400°C – 30 min).

2. Switches

- Molecular switches may be switched by voltage (electricity) or by light (photo switching).
- Electric Switching
  - One of the monomers (building blocks) of a polymer is twisted by applying voltage.
  - Twisting one monomer reduces the charge transfer efficiency along the molecule.
- Photo Switching
  - Some molecules transition from stable (trans) to (cis) configuration under UV light.
  - One of these configurations has high conductance and the other has low conductance which can be used as a switch.

3. Molecular Transistors

- A true transistor effect in a single three-terminal molecule has not been realized yet.
- Molecular transistors may use a single molecule or a monolayer.
- A monolayer transistor is called SAMFET (Self-Assembled Monolayer Field Effect Transistor).
- Monolayer transistor structure
  - Two electrodes (source and drain).
  - Single molecule or monolayer between the source and drain.
  - An underneath gate electrode separated from the structure by a thin dielectric film.
- Single molecule transistor
  - A single molecule is trapped between electrical contacts.
  - A benzene molecule attached to gold contacts could behave just like a silicon transistor.
  - The single molecule transistor is almost binary; it is either ON or OFF.

VI. Conclusion

- Molecular electronics is a potential candidate to replace future CMOS silicon technologies.
- It mainly depends on the self-assembly of monolayers.
- It still faces many challenges such as:
  - Improving reproducibility and repeatability
  - Testing the integration of molecular devices with silicon-CMOS electronics.
  - A true fully molecular 3-terminals device is still lacking.
  - Molecule-electrode coupling strongly modifies the molecular-scale device properties.
  - The interface with the outer-world
  - 3D integration